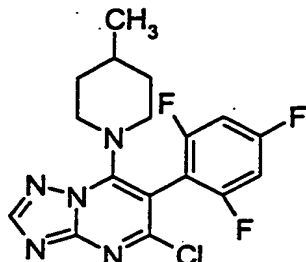


Fungicidal mixtures for controlling rice pathogens

The present invention relates to fungicidal mixtures for controlling rice pathogens, which mixtures comprise, as active components,

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- 1) the triazolopyrimidine derivative of the formula I,



and

- 2) a dithiocarbamate II selected from the group consisting of
manganese-ethylenebis(dithiocarbamate)zinc complex (II.1),
manganese-ethylenebis(dithiocarbamate) (II.2),
zinc ammoniate-ethylenebis(dithiocarbamate) (II.3),
zinc-ethylenebis(dithiocarbamate) (II.4) and
bis(dimethylthiocarbamoyl)disulfide (II.5)

15

in a synergistically effective amount.

Moreover, the invention relates to a method for controlling rice pathogens using mixtures of the compound I with the compounds II and to the use of the compound I with the compounds II for preparing such mixtures and compositions comprising these mixtures.

20

The compound I, 5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, its preparation and its action against harmful fungi are known from the literature (WO 98/46607).

25

The compounds II, their preparation and their action against harmful fungi are known from the literature:

30

- II.1: common name: mancozeb; US 3,379,610
II.2: common name: maneb; US 2,504,404
II.3: common name: metiram; US 3,248,400
II.4: common name: zineb; US 2,457,674
II.5: common name: thiram; DE 642 532.

35

Mixtures of triazolopyrimidine derivatives with mancozeb are known in a general manner from EP-A 988 790. The compound I is embraced by the general disclosure of this publication, but not explicitly mentioned. The combination of compound I with the dithiocarbamates II is novel.

The synergistic mixtures known from EP-A 988 790 are described as being fungicidally active against various diseases of cereals, fruit and vegetables, for example mildew on wheat and barley or gray mold on apples.

It was an object of the present invention to provide, with a view to an effective control of rice pathogens at application rates which are as low as possible, mixtures which, at a reduced total amount of active compounds applied, show improved activity against the rice pathogens.

Owing to the special cultivation conditions of rice plants, the requirements that a rice fungicide has to meet are considerably different from those that fungicides used in cereal or fruit growing have to meet. There are differences in the application method: in addition to foliar application, which is used in many places, in modern rice cultivation the fungicide is applied directly onto the soil during or shortly after sowing. The fungicide is taken up into the plant via the roots and transported in the sap of the plant to the plant parts to be protected. In contrast, in cereal or fruit growing, the fungicide is usually applied onto the leaves or the fruits; accordingly, in these crops the systemic action of the active compounds is considerably less important.

Moreover, rice pathogens are typically different from those in cereals or fruit. *Pyricularia oryzae* and *Corticium sasakii* (syn. *Rhizoctonia solani*) are the pathogens of the diseases most prevalent in rice plants. *Rhizoctonia solani* is the only pathogen of agricultural significance from the sub-class *Agaricomycetidae*. In contrast to most other fungi, this fungus attacks the plant not via spores but via a mycelium infection.

For this reason, findings concerning the fungicidal activity in the cultivation of cereals or fruit cannot be transferred to rice crops.

It was an object of the present invention to provide, with a view to an effective control of rice pathogens at application rates which are as low as possible, mixtures which, at a reduced total amount of active compounds applied, show improved activity against the harmful fungi.

We have found that this object is achieved by the mixtures defined at the outset. Surprisingly, it has been found that the mancozeb mixtures defined at the outset allow considerably better control of rice pathogens than the mancozeb mixtures of the triazolopyrimidine compounds known from EP-A 988 790. Moreover, we have found
 5 that simultaneous, that is joint or separate, application of the compounds I and the compounds II or successive application of the compounds I and the compounds II allows better control of rice pathogens than is possible with the individual compounds.

10 The mixtures of compounds I and II, or the compound I and the compounds II used simultaneously, that is jointly or separately, exhibit outstanding action against rice pathogens from the classes of the *Ascomycetes*, *Deuteromycetes* and *Basidiomycetes*. They can be used for the treatment of seed and as foliar- and soil-acting fungicides.

15 They are especially important for controlling harmful fungi on rice plants and their seeds, such as *Bipolaris* and *Drechslera* species, and also *Pyricularia oryzae*. They are particularly suitable for controlling sheath blight on rice, caused by *Corticium sasakii*.

20 In addition, the combination according to the invention of the compounds I and II is also suitable for controlling other pathogens such as, for example, *Septoria* and *Puccinia* species in cereals and *Alternaria* and *Botrytis* species in vegetables, fruit and grapevines.

25 They can also be used in the protection of materials (e.g. the protection of wood), for example against *Paecilomyces variotii*.

30 When preparing the mixtures, it is preferred to employ the pure active compounds I and II, to which further active compounds against harmful fungi or against other pests, such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active compounds or fertilizers can be added according to need.

Other suitable active compounds in the above sense are in particular active compounds selected from the following groups:

- acylalanines, such as benalaxyl, metalaxyl, ofurace, oxadixyl,
- 35 • amine derivates, such as aldimorph, dodemorph, fenpropimorph, fenpropidin, guazatine, iminoctadine, tridemorph,
- anilinopyrimidines, such as pyrimethanil, mepanipyrim or cyprodinil,
- antibiotics, such as cycloheximid, griseofulvin, kasugamycin, natamycin, polyoxin or streptomycin,

- azoles, such as bitertanol, bromoconazole, cyproconazole, difenoconazole, dinitroconazole, enilconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prochloraz, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizol, triticonazole,
- dicarboximides, such as myclozolin,
- dithiocarbamates, such as ferbam, nabam, metam, propineb, polycarbamat, ziram,
- heterocyclic compounds, such as anilazin, benomyl, boscalid, carbendazim, carboxin, oxycarboxin, cyazofamid, dazomet, dithianon, famoxadone, fenamidone, fuberidazole, flutolanil, furametpyr, isoprothiolan, mepronil, nuarimol, probenazole, pyroquilon, quinoxifen, silthiofam, thiabendazole, thifluzamid, tiadinil, tricyclazole, triforine,
- nitrophenyl derivatives, such as binapacryl, dinocap, dinobuton, nitrophthal-isopropyl,
- phenylpyrroles, such as fenpiclonil or fludioxonil,
- sulfur,
- other fungicides, such as acibenzolar-S-methyl, carpropamid, chlorothalonil, cyflufenamid, cymoxanil, dazomet, diclomezin, diclocymet, diethofencarb, edifenphos, ethaboxam, fenhexamid, fentin-acetate, fenoxanil, ferimzone, fluazinam, fosetyl, fosetyl-aluminum, phosphorous acid, iprovalicarb, hexachlorobenzene, metrafenon, methyl isothiocyanate, pencycuron, propamocarb, phthalid, toloclofos-methyl, quintozone, zoxamid,
- strobilurins, such as azoxystrobin, dimoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, pyraclostrobin or trifloxystrobin,
- sulfenic acid derivatives, such as captan, dichlofluanid, folpet,
- cinnamides and analogous compounds, such as dimethomorph, flumetover or flumorph.

30 In one embodiment of the mixtures according to the invention, a further fungicide III or two fungicides III and IV are added to the compounds I and II.

The active compounds mentioned above are suitable as active compound III in particular for mixtures of the compounds I and II.1 or I and II.3.

35 Particular preference is given to mixtures comprising, as active compound III, a strobilurin, a cinnamide or one of the heterocyclic compounds mentioned above.

40 Other preferred active compounds III are fosetyl, fosetyl-aluminum or phosphorous acid, in particular mixtures comprising the compounds I and II and a component III.

Particular preference is given to mixtures comprising, as active components, the compound I and a compound II.

5 The compound I and the compound II can be applied simultaneously, that is jointly or separately, or in succession, the sequence, in the case of separate application, generally not having any effect on the result of the control measures.

10 The compound I and the compound II are usually applied in a weight ratio of from 100:1 to 1:100, preferably from 5:1 to 1:20, in particular from 1:1 to 1:20.

The components III and IV are added, if appropriate, in a ratio of from 20:1 to 1:20 to the compound I.

15 Depending on the type of compound II and on the desired effect, the application rates of the mixtures according to the invention are from 5 g/ha to 6000 g/ha, preferably from 50 to 2500 g/ha, in particular from 50 to 1000 g/ha.

20 Correspondingly, the application rates for the compound I are generally from 1 to 1000 g/ha, preferably from 10 to 900 g/ha, in particular from 20 to 750 g/ha.

Correspondingly, the application rates for the compound II.1 are generally from 1 to 2000 g/ha, preferably from 10 to 1500 g/ha, in particular from 20 to 750 g/ha.

25 Correspondingly, the application rates for the compound II.2 are generally from 1 to 2500 g/ha, preferably from 10 to 2000 g/ha, in particular from 20 to 1000 g/ha.

Correspondingly, the application rates for the compound II.3 are generally from 1 to 2000 g/ha, preferably from 10 to 1500 g/ha, in particular from 20 to 1000 g/ha.

30 Correspondingly, the application rates for the compound II.4 are generally from 1 to 2000 g/ha, preferably from 10 to 1500 g/ha, in particular from 20 to 1000 g/ha.

Correspondingly, the application rates for the compound II.5 are generally from 1 to 6000 g/ha, preferably from 10 to 3500 g/ha, in particular from 20 to 1000 g/ha.

35 In the treatment of seed, the application rates of the mixture are generally from 1 to 1000 g/100 kg of seed, preferably from 1 to 750 g/100 kg, in particular from 5 to 500 g/100 kg.

In the control of harmful fungi pathogenic to rice plants, the separate or joint application of the compounds I and II or of the mixtures of the compounds I and II is carried out by spraying or dusting the seeds, the seedlings, the plants or the soils before or after sowing of the plants or before or after emergence of the plants. The compounds are preferably applied by spraying the leaves.

The mixtures according to the invention or the compounds I and II can be converted into the customary formulations, for example solutions, emulsions, suspensions, dusts, powders, pastes and granules. The application form depends on the particular purpose; in each case, it should ensure a fine and uniform distribution of the compound according to the invention.

The formulations are prepared in a known manner, for example by extending the active compound with solvents and/or carriers, if desired using emulsifiers and dispersants. Solvents/auxiliaries which are suitable are essentially:

- water, aromatic solvents (for example Solvesso products, xylene), paraffins (for example mineral oil fractions), alcohols (for example methanol, butanol, pentanol, benzyl alcohol), ketones (for example cyclohexanone, gamma-butyrolactone), pyrrolidones (NMP, NOP), acetates (glycol diacetate), glycols, fatty acid dimethylamides, fatty acids and fatty acid esters. In principle, solvent mixtures may also be used.
- carriers such as ground natural minerals (for example kaolins, clays, talc, chalk) and ground synthetic minerals (for example highly disperse silica, silicates); emulsifiers such as nonionic and anionic emulsifiers (for example polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignin-sulfite waste liquors and methylcellulose.

Suitable surfactants are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutyl-naphthalenesulfonic acid, alkylarylsulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates, fatty acids and sulfated fatty alcohol glycol ethers, furthermore condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctylphenol, octylphenol, nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ether, tristyrylphenyl polyglycol ether, alkylaryl polyether alcohols, alcohol and fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lignin-sulfite waste liquors and methylcellulose.

Substances which are suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, cyclohexanol, cyclohexanone, isophorone, strongly polar solvents, for example dimethyl sulfoxide, N-methylpyrrolidone and water.

- 10 Powders, materials for spreading and dustable products can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.

- Granules, for example coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active compounds to solid carriers. Examples of solid carriers are mineral earths such as silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, such as, for example, ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

In general, the formulations comprise from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active compounds. The active compounds are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

The following are examples of formulations: 1. Products for dilution with water

A) Water-soluble concentrates (SL)

10 parts by weight of the active compounds are dissolved in water or in a water-soluble solvent. As an alternative, wetters or other auxiliaries are added. The active compound dissolves upon dilution with water.

B) Dispersible concentrates (DC)

20 parts by weight of the active compounds are dissolved in cyclohexanone with addition of a dispersant, for example polyvinylpyrrolidone. Dilution with water gives a dispersion.

C) Emulsifiable concentrates (EC)

15 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength).

5 Dilution with water gives an emulsion.

D) Emulsions (EW, EO)

40 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength).

10 This mixture is introduced into water by means of an emulsifier (Ultraturrax) and made into a homogeneous emulsion. Dilution with water gives an emulsion.

E) Suspensions (SC, OD)

15 In an agitated ball mill, 20 parts by weight of the active compounds are comminuted with addition of dispersants, wetters and water or an organic solvent to give a fine active compound suspension. Dilution with water gives a stable suspension of the active compound.

F) Water-dispersible granules and water-soluble granules (WG, SG)

20 50 parts by weight of the active compounds are ground finely with addition of dispersants and wetters and made into water-dispersible or water-soluble granules by means of technical appliances (for example extrusion, spray tower, fluidized bed). Dilution with water gives a stable dispersion or solution of the active compound.

25 G) Water-dispersible powders and water-soluble powders (WP, SP)

75 parts by weight of the active compounds are ground in a rotor-stator mill with addition of dispersants, wetters and silica gel. Dilution with water gives a stable dispersion or solution of the active compound.

30 2. Products to be applied undiluted

H) Dustable powders (DP)

5 parts by weight of the active compounds are ground finely and mixed intimately with 95% of finely divided kaolin. This gives a dustable product.

35

I) Granules (GR, FG, GG, MG)

0.5 part by weight of the active compounds is ground finely and associated with 95.5% carriers. Current methods are extrusion, spray-drying or the fluidized bed. This gives granules to be applied undiluted.

5

J) ULV solutions (UL)

10 parts by weight of the active compounds are dissolved in an organic solvent, for example xylene. This gives a product to be applied undiluted.

- 10 The active compounds can be used as such, in the form of their formulations or the use forms prepared therefrom, for example in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dustable products, materials for spreading, or granules, by means of spraying, atomizing, dusting, spreading or pouring. The use forms depend entirely on the intended
- 15 purposes; they are intended to ensure in each case the finest possible distribution of the active compounds according to the invention.

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions,

20 pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of a wetter, tackifier, dispersant or emulsifier. Alternatively, it is possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

25

The active compound concentrations in the ready-to-use preparations can be varied within relatively wide ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

- 30 The active compounds may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active compound, or even to apply the active compound without additives.

Various types of oils, wetters, adjuvants, herbicides, fungicides, other pesticides, or

35 bactericides may be added to the active compounds, if appropriate just immediately prior to use (tank mix). These agents can be admixed with the compositions according to the invention, usually in a weight ratio of 1:10 to 10:1.

The compounds I and II or the mixtures or the corresponding formulations are applied by treating the harmful fungi or the plants, seeds, soils, areas, materials or spaces to be kept free from them with a fungicidally effective amount of the mixture or, in the case of separate application, of the compounds I and II. Application can be carried out before or after infection by the harmful fungi.

The fungicidal action of the compound and the mixtures can be demonstrated by the experiments below:

The active compounds, separately or jointly, were prepared as a stock solution with 0.25% by weight of active compound in acetone or DMSO. 1% by weight of the emulsifier Uniperol® EL (wetting agent having emulsifying and dispersing action based on ethoxylated alkylphenols) was added to this solution, and the solution was diluted with water to the desired concentration.

Use example – Activity against sheath blight on rice caused by *Corticium sasakii*

Pots of rice plants of the cultivar "Tai-Nong 67" were sprayed to runoff point with an aqueous suspension having the concentration of active compound stated below. The next day, oat grains infected with *Corticium sasakii* were placed into the pots (in each case 5 grains per pot). The plants were then placed in a chamber at 26°C and maximum atmospheric humidity. After 11 days, the sheath blight on the untreated but infected control plants had developed to such an extent that the infection could be determined visually in %.

Evaluation is carried out by determining the infected leaf areas in percent. These percentages were converted into efficacies.

The efficacy (E) is calculated as follows using Abbot's formula:

$$E = (1 - \alpha/\beta) \cdot 100$$

α corresponds to the fungicidal infection of the treated plants in % and

β corresponds to the fungicidal infection of the untreated (control) plants in %

An efficacy of 0 means that the infection level of the treated plants corresponds to that of the untreated control plants; an efficacy of 100 means that the treated plants are not infected.

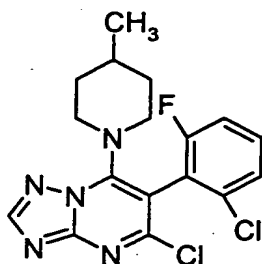
The expected efficacies of the mixtures of active compounds are determined using Colby's formula [R.S. Colby, Weeds 15, 20-22 (1967)] and compared with the observed efficacies.

5 Colby's formula:

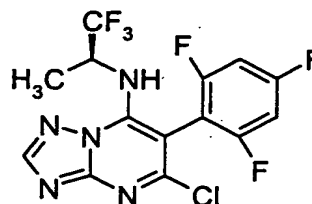
$$E = x + y - x \cdot y / 100$$

- E expected efficacy, expressed in % of the untreated control, when using the mixture of the active compounds A and B at the concentrations a and b
- 10 x efficacy, expressed in % of the untreated control, when using active compound A at the concentration a
- y efficacy, expressed in % of the untreated control, when using active compound B at the concentration b

15 The comparative compounds used were the compounds A and B known from the mancozeb mixtures described in EP-A 988 790:



A



B

Table A – Individual active compounds

Example	Active compound	Concentration of active compound in the spray liquor [ppm]	Efficacy in % of the untreated control
1	control (untreated)	-	(90 % infection)
2	I	4	33
3	II.1 (mancozeb)	16	11
		1	0
4	II.2 (maneb)	16	11
		1	0
5	II.3 (metiram)	16	22
		1	0
6	II.5 (thiram)	16	0
		1	0
7	Comparative compound A	4	0
6	Comparative compound B	4	67

Table B – Mixtures according to the invention

Example	Mixture of active compounds; concentration; mixing ratio	Observed efficacy	Calculated efficacy*)
9	I + II.1 4 + 1 ppm 4:1	78	33
10	I + II.1 4 + 16 ppm 1:4	100	41
11	I + II.2 4 + 1 ppm 4:1	83	33
12	I + II.2 4 + 16 ppm 1:4	94	41
13	I + II.3 4 + 1 ppm 4:1	89	33
14	I + II.3 4 + 16 ppm 1:4	94	48
15	I + II.5 4 + 1 ppm 4:1	89	33
16	I + II.5 4 + 16 ppm 1:4	91	33

*) efficacy calculated using Colby's formula

Table C – Comparative tests

Example	Mixture of active compounds; concentration; mixing ratio	Observed efficacy	Calculated efficacy*)
17	A + II.1 4 + 1 ppm 4:1	11	0
18	A + II.1 4 + 16 ppm 1:4	22	11

Example	Mixture of active compounds; concentration; mixing ratio	Observed efficacy	Calculated efficacy*)
19	A + II.2 4 + 1 ppm 4:1	0	0
20	A + II.2 4 + 16 ppm 1:4	11	11
21	A + II.3 4 + 1 ppm 4:1	11	0
22	A + II.3 4 + 16 ppm 1:4	33	22
23	A + II.5 4 + 1 ppm 4:1	22	0
24	A + II.5 4 + 16 ppm 1:4	33	0
25	B+ II.1 4 + 1 ppm 4:1	67	67
26	B+ II.1 4 + 16 ppm 1:4	67	70
27	B+ II.2 4 + 1 ppm 4:1	67	67
28	B+ II.2 4 + 16 ppm 1:4	67	70
29	B+ II.3 4 + 1 ppm 4:1	56	67
30	B+ II.3 4 + 16 ppm 1:4	67	74

Example	Mixture of active compounds; concentration; mixing ratio	Observed efficacy	Calculated efficacy*)
31	B+ II.5 4 + 1 ppm 4:1	67	67
32	B+ II.5 4 + 16 ppm 1:4	56	67

*) efficacy calculated using Colby's formula

5 The test results show that, owing to strong synergism, the mixtures according to the invention are considerably more effective than the dithiocarbamate mixtures of the comparative compounds known from EP-A 988 780.